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Present Uses of Chlorofluorocarbons and Effects Due to Environmental Regulations[1]

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The paper deals with the expected impact of the safety and environmental issues concerning the use of chlorofluorocarbons and presents a status report on alternative compounds under development.

KEY WORDS: aerosols; blowing agents; chlorofluorocarbons; cleaning agents; refrigerants.

1. INTRODUCTION

This paper deals with the present uses of chlorofluorocarbons and effects due to environmental regulations. First, a brief overview is provided of the key market segments and end uses of chlorofluorocarbons (CFCs). Then, the expected impact of regulations on the CFC producing and using industries is discussed. Finally, a status report on alternative products now under development is provided.

2. PRESENT USES OF CFCs

CFCs have played an important role in many of the social, demographic, and technological changes and advancements that have occurred in the United States over the last 50 years. For example, the demographic growth in the Sun Belt, an increasingly mobile population, and construction of vast indoor office, retail, and recreational complexes all were made possible because of the availability of relatively inexpensive air

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conditioning technology afforded by CFCs. In the United States, 75% of the food eaten depends on the use of CFC refrigerants at some point in the production and distribution chain. Also, the era of computerization and the rapid miniaturization of electronic parts have been greatly enhanced by the cleaning capabilities of CFC solvents. And CFCs are important as blowing agents in making insulating, food packaging, and cushioning foams from plastic materials.

In the United States alone, CFCs are used by some 5000 businesses at nearly 375,000 locations to produce goods and services worth more than $28 billion a year. CFC-related jobs total 715,000. The estimated value of installed products relying on CFCs is more than $135 billion.

3. IMPACT OF REGULATIONS

Unilateral action to control CFCs in the United States would have a significant disruptive impact on many key U.S. industries, industries that contribute to the quality of life in the United States and enhance our position in the global economy. Actually, the United States initiated unilateral action on CFCs in the late 1970s, singling out aerosols. This action received little support from other major CFC users around the world. A better solution was needed, one that addressed the environmental need while recognizing societal needs as well.

In our view and that of many others, the answer is the Montreal Protocol, signed in Montreal in September 1987. The protocol's key provisions call for

(a) a consumption freeze in mid-1989, at 1986 levels—consumption is defined in the protocol as production plus imports minus exports;

(b) a 20% reduction in mid-1993; and

(c) an additional 30% reduction in mid-1998.

The impact of these cutbacks will be significant, primarily because demand for CFCs has been growing rapidly. In the absence of restrictions or environmental concern, CFC use could have been expected to grow by 48% from 1986 to 1999 and 119% from 1986 to 2010.

Du Pont is committed to an orderly transition to the total phaseout of fully halogenated CFCs by the end of the century. We also are urging all nations to accelerate ratification of the Montreal Protocol and then immediately initiate the protocol's assessment process to consider additional steps that would accomplish a total phaseout in a timely manner. We believe that with the cooperation of all nations and the producer and user industries, an additional protocol step providing for future phaseout of fully halogenated CFCs is an achievable goal. Because of the basic societal needs dependent on CFCs, the introduction of alternative chemicals and technologies will be essential to an orderly phaseout.

4. DEVELOPMENT OF ALTERNATIVES

Next we discuss the development of alternatives, using Du Pont's program as an example of the many industry efforts now underway.

Du Pont will spend well in excess of $30 million this year (1988) to support R&D for process development, market research, and applications testing. An additional $30 million in capital funds was authorized this year. The program goal is to ensure that these products perform well, are compatible with customer equipment and processes, are acceptable from a value-in-use standpoint, and above all, are environmentally acceptable.

The leading candidates for the major uses of CFC-11 and CFC-12 are HCFC-22, which is already commercially available, and new products HFC-134a, HCFC-123, and HCFC-141b. These compounds were identified by Du Pont in 1980 and our results were shared with the rest of industry.

A key element in our evaluation program is an assessment of the ability of the candidate compound to meet stringent toxicology requirements and be produced in commercial quantities at a price society is willing to pay. Efforts to date have identified potential commercial routes to HFC-134a, HCFC-123, and HCFC-141b. Currently pilot plants for all three compounds are making developmental quantities. The goal is to produce sufficient material for toxicity tests and process development and, also, to have adequate quantities available for customer evaluation.

5. TESTING OF TOXICITY

Fourteen CFC producers have joined forces through the Program for Alternative Fluorocarbon Toxicity Testing to conduct the needed toxicity tests on the new compounds. To avoid duplicative testing, a panel of industrial toxicologists has developed a test schedule which calls for a battery of preliminary tests to be conducted simultaneously. This will lay the foundation for more extensive testing.

Although the test programs are not expected to be completed for about 5 years, this is an ambitious schedule—much shorter than the average 6 to 7 years for typical toxicity testing programs.

6. TIMETABLE

Du Pont's vision of an expedited commercialization timetable is embodied in the schedule which follows. Du Pont's process development work for the leading candidates should be completed by 1990. Preliminary plant-design work to identify the manufacturing process has started and design completion is anticipated between 1990 and 1991.

To meet this schedule, an investment decision has to be made prior to the receipt of final toxicology data. We will have to rely on the preliminary data, as will our customers, in determining whether the identified substitutes are feasible as commercial candidates to begin taking major financial risks.

If the process development and plant-design phases program are successful and corporate authorization is received, it is anticipated that capital could be committed and the construction of world-scale facilities could be started as early as 1990. Since we are compressing these design and construction related activities, construction could be delayed if we cannot complete plant design or specify process equipment that requires a long lead time for ordering or if toxicity testing results eliminate a candidate product from consideration.

Du Pont's goal is to commercialize a series of alternative products during a 3- to 5-year period beginning in 1990. This schedule assumes successful development of commercial manufacturing processes, favorable toxicology results, and strong market demand.

For applications testing, we are now providing samples of the leading candidates. As we gain experience in pilot plant and small-scale facilities, larger quantities will be made available for needed applications work and toxicology research. We have cooperative testing arrangements with many of the leading user industry companies.

7. SUBSTITUTES FOR END USES

7.1. Refrigerants

For refrigeration applications, the primary candidates are HFC-134a and HCFC-123. Small-scale process scouting plants are now operating. Du Pont anticipates early introduction and prompt adoption by OEMs (original equipment manufacturers) to permit the remaining CFC-11 and CFC-12 to be available for aftermarket needs.

As long-term replacements for R-12, Du Pont has identified R-22 and R134a. Each alternate would require a change in existing systems. For example, since R-22 is a higher-pressure refrigerant than R-12, its use would require major system redesign. R-134a operates at pressures only slightly higher than R-12, but new refrigerant oil, system elastomers, and expansion devices may be needed.

Du Pont is actively pursuing the development of an economical process to produce R-134a; even if we are successful, large-scale commercialization is several years away. If production of R-134a eventually reaches production rates similar to the current rates for R-12, the cost would likely be three to five times the cost of R-12. Preliminary testing indicates that R-134a has safety characteristics similar to those of R-12 and R-22. However, much more testing is required before firm conclusions can be reached.

As a replacement for R-11, Du Pont has identified R-123. Studies are under way to determine what changes would be needed to an existing system to use R-123. Most likely, OEMs must complete testing in their specific equipment and then approve modifications.

For all potential refrigerants, an accurate determination of pressure–temperature relationships and temperature-dependent oil solubility and information on thermal decomposition are needed. In some cases, one may also consider blends and azeotropes, for which we will need accurate vapor–liquid equilibrium data.

7.2. Blowing Agents

Du Pont's focus for blowing-agent alternatives is to identify candidates that are safe, nonflammable, and nonreactive and have a low order of toxicity. We are at different stages of development for different products and applications.

To replace CFC-11 in polyurethanes and phenolic foams, HCFC-123 appears to be the most promising candidate. HCFC-141b also has potential and could probably be made available more quickly in commercial quantities but is slightly flammable. Both products are still some time away from commercial availability and their toxicity is under review. Applications testing for both products shows real promise, however, and a key question is whether users will accept a flammable product such as HCFC-141b, which is likely to be less expensive to use than HCFC-123.

To replace CFC-12 in polystyrene and for polyurethane frothing, HCFC-22 and HFC-134a appear to be the best candidates. While HFC-134a best matches CFC-12 from the standpoint of boiling point and vapor pressure, the uncertainty of when it will be available and its high estimated cost (three to five times higher than CFC-12 at high production rates) greatly reduce its attractiveness for these markets. The search for other viable candidates is being continued.

HCFC-22 has the lowest cost of the potential alternatives (1.5 times CFC-12) and is already produced commercially. It also offers a low order of acute and chronic toxicity. HCFC-22 has been used successfully to produce polystyrene foam sheet in the United States. It was recently announced that we would market a highly purified grade of HCFC-22 in the United States under the Formacel S-Food Grade trademark for all polystyrene foam applications, including food trays and fast-food containers.

Other products which might be used in blowing-agent segments are the existing products HCFC-142b and HFC-152a and the new product HCFC-124. Work is under way to determine their applicability.

To explore blowing-agent applications fully, the pressure–temperature relationships and solubilities, as well as a good measure of flammability ranges for the flammable compounds, need to be known. For insulation applications, heat-transfer coefficients for both the blowing agents and the end-product foams are important.

7.3. Cleaning Agents

Du Pont has a research and development program targeted for CFC-113 replacements, with several candidates under development. Their applications, toxicity, and manufacturing processes are currently being determined. The primary thermophysical property needs for cleaning agents are vapor pressures and solubilities.

The objective in the development of these candidates is to provide a product line functionally equivalent to CFC-113-based cleaning agents while striving to minimize the changes that a CFC-113 user would experience. The goal is to have developmental samples available in 1989.

While this effort is under way, we intend to supply CFC-113 to our customers to permit an orderly transition to alternatives. In addition, we will work closely with customers to conserve product and encourage the use of Freon SMT and Freon MCA as a transition to more environmentally acceptable compounds. In initial tests, Freon SMT has proven to be a very effective cleaning agent. Although it contains CFC-113, its ozone depletion potential is about 25% less that of our current product line. Freon MCA has an ozone-depletion potential 37% less than that of CFC-113.

7.4. Aerosols

There are several options currently available as replacements for CFC aerosol propellants; Du Pont markets these new propellants under the

Dymel trademark. These products include dimethyl ether (DME), HCFC-22, HCFC-142b, and HFC-152a. HCFC-22 is the only nonflammable propellant for general usage; it is used in combination with other flammable components to create nonflammable mixtures and azeotropes. Knowledge of vapor pressures for a variety of mixtures of common components will be necessary, but these are typically studied only for individual product formulations.

All of these alternatives have undergone extensive toxicity studies and all have a 1000-ppm TWA (8-time-weighted average) in the United States. Extensive animal studies have shown that these propellants pose no hazard to people relative to systemic toxicity, carcinogenicity, mutagenicity, or teratogenicity at or below the occupational exposure limit (TWA) of 1000 ppm.

7.5. Halons

Du Pont is currently using at an existing product, Halon-121 (HCFC-22), as an alternative agent for discharge testing. The product shows promise in that it exhibits similar properties to Halon-1301 and, thus, may be a viable simulant for testing Halon systems. In fact, Du Pont will stop using Halon-1301 as a testing agent by the end of this year.

Although the efforts continue to identify an alternate for the Halon-1301 fire extinguishant, we are not optimistic. In the interim, Du Pont will continue to promote reduction of nonessential emissions.

8. CONCLUDING REMARKS

It is important to pay serious attention to safety and environmental issues related to the use of working fluids in technical applications. From our standpoint, eliminating one potential risk—long-term depletion of the ozone layer—by taking on unknown or potentially greater risks—using replacement products that have not been proven safe for humans and the environment—is not acceptable. The overriding goal must be overall reduction of risk. And that is industry's goal in striving for an orderly transition to safe and effective alternative products.

By building on the growing international scientific consensus, worldwide policy makers are in a position to act cooperatively, not unilaterally, in striving to reach this goal. Unless the transition from CFCs to alternate products is carefully planned on an international scale, significant social and commercial disruptions could occur. A successful transition will require the dedication, cooperation, and hard work of government, industry, and the public in all nations.

Du Pont continues to urge a global solution to the CFC/ozone issue and remains committed to the protocol as the most effective process for addressing the issue. Only a cooperative effort ensure that the environment is protected for the benefit of future generations.